A NEW APPROACH TO MERCURY SPECIATION IN SOLIDS USING A THERMAL DESORPTION TECHNIQUE

Marta Rumayor, M. Antonia Lopez-Anton*, Mercedes Díaz-Somoano,
M. Rosa Martínez-Tarazona

Instituto Nacional del Carbón (CSIC), Francisco Pintado Fe, 26, 33011, Oviedo, Spain

*Corresponding author:

Phone: +34 985 119090
Fax: +34 985 297662
Email: marian@incar.csic.es

Abstracts

Identification of the chemical form of mercury in coals and during the entire combustion process is essential for successfully controlling mercury emissions. However, the speciation of mercury in coal and, in general, in carbonaceous samples has so far proved elusive because of the limitations of current analytical techniques as a consequence of the detection limits of the equipment or interferences originating from the matrix. In this work a new device based on temperature programmed desorption (HgTPD) has been developed to identify mercury species in carbonaceous materials. The samples studied were coals of different rank obtained from around the world and activated carbons that had previously been used as mercury sorbents in simulated coal combustion atmospheres. The mercury species present in both types of sample were identified without any interference from the matrix. This achievement is extremely important as it will contribute to a better understanding of (i) the behavior of mercury species in coal in coal utilization processes and (ii) the retention mechanisms and subsequent stability of the mercury species captured by carbon sorbents.

Keywords: mercury; speciation; coal; thermal analysis

1. Introduction

Mercury is a global pollutant because it can be transported over long distances through the atmosphere. The ability to determine the chemical form of mercury in a contaminated and industrial environment is the key to predicting its solubility, transport, behavior and bioavailability as well as for designing effective control and remediation technology.

The current interest in the analysis of mercury species in coals and activated carbons is a consequence of the need to control mercury pollution from coal combustion processes. Mercury is a naturally occurring element in coal. Although the speciation of this element has often proved elusive due to the limitations of the instruments designed for this task, it is believed that mercury can be present in coals as sulphides (HgS), selenides (HgSe), in forms associated with pyrite and sphalerite ($HgFeS_2$), organically bound to coaly matter (HgOM), or even as metallic mercury (Hg^0) [1, 2]. The concentrations of mercury in coal generally range from 0.02 to 1.0 $\mu g \cdot g^{-1}$ [1, 2]. However, the huge amount of this combustible consumed for power generation makes coal combustion power plants one of the largest sources of mercury emissions to the atmosphere. 475 tons of mercury were emitted in 2010 to the air from these utilities [3]. The reduction of mercury emissions from coal combustion can be tackled in different ways. It can be achieved by cleaning the coal [4-7] or by thermal drying [8] as a previous step to its combustion, by optimizing control systems used for other pollutants [9], or by developing specific mercury control strategies such as the retention of the mercury present in the flue gas by solid sorbents [10, 11]. In the case of the pre-combustion methods, the mode of occurrence of mercury in the coal will determine the

efficiency of the process. In the same framework, the speciation of mercury in sorbents used for mercury retention is also necessary to understand the interactions that occur between the mercury species in gas phase and the material used for its retention.

With the analytical equipment now available, determination of the total mercury content in solid samples at $\mu g \cdot g^{-1}$ and even at $\mu g \cdot kg^{-1}$ levels can be easily and cost-effectively carried out. The most sensitive and accurate techniques are based on using atomic absorption spectrophotometry and atomic fluorescence detection [12]. However, it is still difficult to identify the mode of occurrence of mercury in all types of solids. X-ray adsorption fine structure spectroscopy (EXAFS) [13, 14], sequential extraction (SE) [15, 16] and temperature programmed desorption (HgTPD) [17-22] are the techniques usually employed to identify mercury species in solids. However, all of them have their limitations especially when they are applied to samples with a high content of carbonaceous matter and low concentrations of mercury. The high detection limit in the case of EXAFS, the low selectivity and inability to extract individual mercury species of SE and the interferences caused by volatile matter in HgTPD are the main problems that arise in carbon materials analysis. For these reasons, it is necessary to develop sensitive and selective methods of analysis that are free from interference and applicable to any material. In the case of HgTPD, optimization of the techique entails solving the problems associated with the matrix effects and especially those related to carbonaceous matter.

The aim of the present study is to identify mercury species in solids with a high carbon content using a novel thermal desorption technique. For this purpose, a commercial thermo-desorption device was modified to oxidise the volatile matter produced by carbon materials without interfering with the evaporated mercury species. The samples studied were coals with different characteristics and activated carbons

101 previously used as mercury sorbents in simulated coal combustion and oxy-combustion
102 atmospheres.
103
104 **2. Material and methods**
105 *2.1. Samples*
106 Eighteen coal samples of different origin were chosen for the identification of
107 mercury species by a modified thermal desorption method (Table 1). The coal ranks
108 included lignites (4 samples), sub-bituminous (1 sample), bituminous (11 samples) and
109 anthracites (2 samples).
110 Moreover, two commercial activated carbons (Norit RB3 and RBHG3), previously
111 used as mercury sorbents in simulated coal combustion and oxy-combustion
112 atmospheres [23], were analysed by the same method. RBHG3 was prepared by
113 impregnating RB3 with sulphur compounds to be used for mercury retention at low
114 temperatures [24].
115
116 *2.2. Experimental device for mercury speciation*
117 For this study a specially designed procedure based on thermo-desorption was
118 developed and optimized for mercury speciation in carbonaceous materials [25] (Figure
119 1). The speciation device employed was a modification of a commercial device
120 described by the authors elsewhere [21]. The main components of the commercial
121 apparatus are a furnace (PYRO 915) and a mercury analyzer (Lumex RA-915). In this
122 equipment, mercury is evaporated from the solid during combustion and decomposition
123 in the oven where reduction to elemental mercury also takes place. The elemental
124 mercury (Hg^0) in gas phase is transported to the analyzer where it is detected as $Hg^0(g)$.
125 This apparatus records temperature versus mercury and is not only able to determine the

126 total concentration of mercury in the solid samples but also to identify the species of
127 mercury. For this purpose, it was first necessary to analyze different mercury standards
128 with different temperatures of decomposition. By comparison it would then be possible
129 to identify the mercury species in the solid samples. Commercial devices usually work
130 with air or oxygen to facilitate the total decomposition of the solids. However, these
131 gases can interfere with some of the mercury species. To overcome this problem a new
132 device was developed. The modified device was set up by coupling a second thermo-
133 desorption furnace to a commercial PYRO 915 furnace and then connecting these to a
134 commercial continuous mercury analyser (Lumex RA-915).

135 The novelty of this set-up is that the desorption of the mercury species takes place
136 in an inert atmosphere (N_2) in the new furnace at the beginning of the process to avoid
137 interferences and undesired reactions, while at the same time O_2 is introduced into the
138 commercial furnace PYRO in order to oxidize the volatile matter emitted by the carbon
139 material. The new furnace contains two chambers, in the first of which the desorption
140 of the mercury species occurs, while the second chamber ensures that the temperature is
141 maintained so as to avoid cool zones and the condensation of the mercury until it enters
142 the PYRO furnace. The new furnace also contains two temperature controllers that
143 allow the heating ramp and the temperature in the zone between the new and PYRO
144 furnace to be optimized. First the sample is weighed and then introduced into the new
145 thermo desorption furnace. The temperature of the sample is continuously controlled by
146 a thermocouple situated inside a quartz sample boat. In the new thermo-desorption
147 furnace the mercury compounds are released from the solid matrix in a flow of nitrogen
148 of 500 $mL \cdot min^{-1}$ under a controlled heating mode of 50 $^{o}C \cdot min^{-1}$. The PYRO 915 unit is
149 kept at 800 ^{o}C in a flow of oxygen of 500 $mL \cdot min^{-1}$. This unit serves to decompose
150 volatile matter and to reduce the mercury compounds to elemental mercury. Finally, the

151 Hg^0 is determined using a RA-915+ analyser based on differential Zeeman atomic
152 absorption spectrometry.

153 The mercury species are identified from the high peak temperature at which they
154 are released. To this end, the desorption profiles are compared with the desorption
155 profiles of the reference mercury compounds that are the most likely species to form in
156 coals [HgS, HgSe Hg-OM, (organic matter) and Hg-FeS_2] . The presence of HgO and
157 $HgCl_2$ was also considered to be possible in coals and activated carbons. The reference
158 compounds for mercury sulfide, mercury selenide, mercury oxide and mercury chloride
159 were prepared from commercially pure HgS, HgSe, HgO and $HgCl_2$, respectively,
160 which were blended with silica and carbon matrices in mercury concentrations of up to
161 10 $mg \cdot kg^{-1}$. The mercury standard for organic matter (Hg-OM) was prepared from a
162 humic acid [26]. Humic acids contain COOH, OH and CO groups and, although the
163 presence of these groups will depend on coal rank, a similar environment for the
164 mercury linkages in humic acids and carbon materials can be considered as likely. On
165 the basis of this premise, mercury bound to humic acid was chosen as being
166 representative of organic groups in coals [1, 27]. Finally, a sample of natural pyrite
167 (FeS_2) was used as the reference compound for mercury associated to pyrite (Hg-FeS_2).

168 Overlapping peaks were deconvoluted using Origin 6.0 software. The accuracy and
169 precision of the analysis of the reference mercury compounds was validated by means
170 of 5 analyses of one of the reference samples (HgS). The results showed differences in a
171 range of 15-20% between the total mercury concentrations obtained from calculation of
172 the peak area (experimental) and the expected concentrations, whereas the relative
173 standard deviation (%RSD) was lower than 10%.

174

175 **3. Results and discussion**

176 *3.1. Mercury speciation in coal samples.*

177 The combustibles analyzed in this work are, in most cases, coals or coal blends
178 used to feed thermal power plants. As explained above, this study aims to validate a
179 technique based on thermal desorption for the identification of different mercury species
180 in carbonaceous samples. It is not intended to be an evaluation of the origin of mercury
181 in coal. However, a collateral result of this study is that it does provide useful
182 information about the mode of occurrence of mercury in coals of different
183 characteristics. It is therefore important to take into account some of the characteristics
184 of these samples such as the S, Se and Cl whose contents are presented in Table 1. The
185 affinity of mercury for these elements is well-known. In general, the mercury
186 concentration in the coals ranges from 0.08 to 0.3 μg g^{-1}, with the exception of the
187 bituminous coal SB-Jo which contains 1.5 μg g^{-1}. The chlorine content is <150 μg g^{-1}
188 with the exception of two bituminous coals (SB-Ca and SB-Mo) and one anthracite
189 (SA-T) whose chlorine contents range between 700 and 950 μg g^{-1}. The sulphur content
190 ranges from 0.3 to 5 % while that of selenium ranges from 0.1 to 7 μg g^{-1}.

191 Figures 2-4 show the mercury desorption profiles for all the coal samples grouped
192 according to their rank: lignites (Figure 2), bituminous and subbituminous coals (Figure
193 3) and anthracites (Figure 4). As can be seen, mercury is mainly released between 100
194 and 500ºC from lignite, bituminous and subbituminous coals and up to 600ºC from
195 anthracites. According to the thermal desorption data of the mercury reference
196 compounds (Table 2), the main mercury species in this temperature range can be
197 expected to be mercury bound to organic matter (Hg-OM), mercury associated to pyrite
198 (Hg-FeS_2) and HgS, the most abundant mercury mineral in the Earth`s crust. In
199 addition, mercury is also present as HgSe in bituminous coals. Others species such as
200 HgO or even $HgCl_2$ might also occur in some coals but in lower proportions (Table 3).

201 The presence of these species could be a consequence of reactions in the environment of
202 the coalfield and transformations brought about by percolated species.
203 As can be seen in Figure 2 the HgTPD obtained from the lignites shows a double
204 maximum peak between 168 and 220ºC. The peak at 169ºC corresponds to Hg-FeS_2
205 whereas the peak at 220ºC is assigned to Hg-OM. Morover in some samples the
206 presence of $HgCl_2$ cannot be ruled out since a small shoulder is observed at
207 approximately 130º. This species is not abundant but it might be incorporated into coaly
208 matter under favourable environmental conditions.
209 The presence of organic mercury (Hg-OM) is more probable in low rank coals,
210 where coaly matter contains more functional groups (Figures 2-3), than in more evolved
211 high rank coals (Figure 4), where functional groups have been lost. Indeed, the main
212 peak observed in the anthracites studied (Figure 4) is at approximately 300ºC,
213 corresponding mainly to sulphides (Table 1), whereas the peak corresponding to Hg-
214 OM is less significant.
215 The HgTPD method developed in this work was found to be highly effective for
216 identifying mercury species in coals. Although the number of coals analysed may not
217 represent all the different types of coal, the results obtained do permit a few
218 generalizations. The main species present in lignites is Hg-OM and mercury linked to
219 pyrite (Hg-FeS_2). In subbituminous and bituminous coals there is a contribution by both
220 organic matter and sulphides, where some HgSe is also present in conjunction with a
221 small amount of $HgCl_2$ and HgO in some cases. Sulphides and HgO are the main
222 mercury species present in the anthracites. It should be pointed out that in the samples
223 evaluated in this work the majority of the mercury species expected to be present in the
224 coals were identified.
225

226 *3.2. Mercury speciation in activated carbon sorbents*

227 A well-known technology used to control mercury emissions in energy generation
228 from coal combustion is the injection of activated carbon [28]. The efficiency of
229 mercury retention in activated carbons varies depending on the type of carbon, coal and
230 combustion conditions [10, 29].

231 The activated carbons employed in this study for the identification of mercury
232 species (RB3 and RBHG3), have been tested previously in various conditions and have
233 been used as reference materials for mercury capture [23, 24, 30]. On the basis of the
234 knowledge acquired about the characterisics of these activated carbons and their
235 behavior as mercury sorbents, the HgTPD method can now be used to identify the
236 mercury species formed in the retention process under several conditions. The
237 identification of the species present in these sorbents after mercury retention will
238 contribute not only to our understanding of the mercury retention mechanism in
239 activated carbons but also explain the leaching of mercury species from activated
240 carbon wastes.

241 The commercial activated carbons used for this study had been previously tested in
242 a laboratory scale reactor by our group [23]. The sorbents were employed in three
243 different atmospheres; an inert atmosphere (N_2) and under simulated oxy-combustion
244 and air combustion flue gas flows. When the sorbents after retention are analyzed by
245 HgTPD, the different mercury species retained in the N_2, oxy-combustion and air
246 combustion atmospheres may be identified and the effect of the gas composition may be
247 evaluated. The results of mercury retention capacities were presented in a previous work
248 [23], the main conclusions of which were as follows: i) in the N_2 atmosphere, RBHG3
249 retained Hg^0 with an efficiency of almost 100%, whereas RB3 showed a negligible Hg^0
250 retention capacity; ii) in the oxy-combustion atmosphere, the mercury retention capacity

of RBHG3 was lower (4%) than that observed in the N_2 atmosphere and similar to that of RB3 (6%); and iii) in the air combustion atmosphere, the mercury retention capacities of RB3 and RBHG3 were similar to that observed in the oxy-combustion atmosphere, i.e., the concentration of CO_2 and H_2O did not affect the mercury retention capacity as long as the concentrations of the other gases remained the same in the both atmospheres. These conclusions refer to the total amount of mercury retained. The novelty of the present study is that thanks to the HgTPD method developed for this study it was also possible to identify the mercury species formed in the sorbent.

Figures 5-6 show the profiles of mercury desorption for RB3 and RBHG3 in the N_2, oxy-combustion and air combustion atmospheres. According to the high-peak temperatures for the reference compounds (Table 2), the species retained in the activated carbons under oxy-combustion and air combustion conditions was mainly Hg-OM (peak at approximately 200ºC), whereas in the N_2 atmosphere the main species identified was HgS (represented by a peak at 300ºC). From these results it is inferred that in a N_2 atmosphere, mercury that remains as Hg^0, reacts with the sulphur present in the carbon to yield HgS. It should be borne in mind that the sulphur contents of RB3 and RBHG3 are 0.4 and 6%, respectively [24]. Thus, the proportion of mercury retained in N_2 in RB3 is insignificant compared to the amount retained in RBHG3.

Mercury retention by RB3 and RBHG3 in the oxy-combustion and air combustion atmospheres occurs via the linkage of mercury to organic matter (desorption peak at 220 ºC) (Figures 5-6). This is a consequence of the homogeneous and heterogeneous oxidation of Hg^0 in these atmospheres and the subsequent linkage of reactive oxidized mercury (Hg^{2+}) to the carbon matter. In a previous study carried out by the authors with the same activated carbons [23] at least 80% of the Hg^{2+} resulting from homogeneous and heterogeneous oxidation was observed in both atmospheres. Therefore, the results

obtained by thermal desorption confirm that the main mechanism of mercury retention in both sorbents in the oxy-combustion and air combustion atmospheres is via the oxidation of mercury and its subsequent adsorption onto the carbon surface, whereas in an inert atmosphere, where mercury is as Hg^0, interaction mainly occurs through the formation of HgS.

4. Conclusions

A new device based on thermal desorption was developed in this work to identify mercury species in carbonaceous samples. The results were found to be very promising for differentiating mercury species in the type of samples chosen for this study. The results confirm that different mercury species are present in coals of different characteristics. The mercury species found in the lignite and bituminous coals were mainly associated to organic matter and/or pyritic sulphur, whereas in the anthracites, the mercury species were mainly associated to sulphur.

Moreover, the mercury thermal desorption technique (HgTPD) was found to be a useful tool for clarifying the mechanism of reaction between the mercury and the activated carbons employed as sorbents in different coal combustion conditions since it served to identify the mercury species retained. In an inert atmosphere, where mercury remains as Hg^0, this species is captured as HgS, whereas in a combustion atmosphere where a significant proportion of the mercury is oxidized (Hg^{2+}), organic linkage to carbon material is the most frequent form of retention.

Acknowledgments

300 The authors are grateful to the National Research Program under project CTM2011–
301 22921 and thank the Spanish Research Council (CSIC) for awarding Ms. Marta
302 Rumayor a JAE-predoc fellowship.
303

304 **References**

305 [1] Yudovich YaE, Ketris MP. Mercury in coal: a review: Part 1. Geochemistry. Int J
306 Coal Geol 2005;62(3):107-134.

307 [2] Swaine DJ. Trace elements in coal. Butterworth, London. 1990. p. 276

308 [3] UNEP. Global Mercury Assessment 2013: Sources, Emissions, Releases
309 and Environmental Transport. UNEP Chemicals Branch, Geneva, Switzerland, 2013.

310 [4] López-Antón MA, Díaz-Somoano M, García AB, Martínez-Tarazona MR.
311 Evaluation of mercury associations in two coals of different rank using physical
312 separation procedures. Fuel 2006;85:1389-1395.

313 [5] Martínez-Tarazona MR, García AB. Trace elements removal during coal cleaning
314 by froth flotation. In: Elemental analysis of coal and by-products. World Scientific.
315 1991. p. 295-8.

316 [6] García AB, Vega JMG, Martínez-Tarazona MR, Spears DA. The removal of trace
317 elements from Spanish high rank coals by a selective agglomeration process. Fuel
318 1994;73:1189-1196.

319 [7] Toole-O'Neil B, Tewalt SJ, Finkelman RB, Akers DJ. Mercury concentration in coal
320 - unraveling the puzzle. Fuel 1999;78:47-54.

321 [8] Bland AE, Greenwell C, Newcomer J, Sellakumar KM, Carney BA. A novel
322 pathway for mercury removal by thermal treatment of coal. Presented at the 33rd

323 International Technical Conference on Coal Utilization & Fuel Systems, Clearwater,
324 FL, June 1-5, 2008.

325 [9] Ochoa-González R, Díaz-Somoano M, López-Antón MA, Martínez-Tarazona MR.
326 Effect of adding aluminium salts to wet FGD systems upon the stabilization of mercury.
327 Fuel 2012;96:568-571.

328 [10] Sjostrom S, Durham M, Bustard CJ, Martin C. Activated carbon injection for
329 mercury control: Overview. Fuel 2010;89:1320-1322.

330 [11] Fuente-Cuesta A, Lopez-Anton MA, Diaz-Somoano M, Martinez-Tarazona MR.
331 Retention of mercury by low-cost sorbents: Influence of flue gas composition and fly as
332 occurrence. Chem Eng J 2012;213:16-21.

333 [12] López-Antón MA, Díaz-Somoano M, Ochoa-González R, Martínez-Tarazona MR.
334 Analytical methods for mercury analysis in coal and coal combustion by-products. Int J
335 Coal Geol 2012;94:44-53.

336 [13] Huggins FE, Yap N, Huffman GP, Senior CL. XAFS characterization of mercury
337 captured from combustion gases on sorbents at low temperatures. Fuel Process Technol
338 2003;82:167-196.

339 [14] Kim CS, Rytuba JJ, Brown GE. EXAFS study of mercury(II) sorption to Fe- and
340 Al-(hydr)oxides: I. Effects of pH. J. Colloid Interface Sci 2004;271(1):1-15.

341 [15] Rumayor M, Diaz-Somoano M, Lopez-Anton MA, Martinez-Tarazona MR.
342 Application of thermal desorption for the identification of mercury species in solids
343 derived from coal utilization. Chemosphere 2015;119:459-465.

344 [16] Biester H, Scholz C. Determination of Mercury Binding Forms in Contaminated
345 Soils: Mercury Pyrolysis versus Sequential Extractions. Environ Sci Technol
346 1996;31:233-239.

347 [17] Biester H, Gosar M, Covelli S. Mercury Speciation in Sediments Affected by
348 Dumped Mining Residues in the Drainage Area of the Idrija Mercury Mine, Slovenia.
349 Environ Sci Technol 2000;34:3330-3336.

350 [18] Reis AT, Coelho JP, Rodrigues SM, Rocha R, Davidson CM, Duarte AC, Pereira
351 E. Development and validation of a simple thermo-desorption technique for mercury
352 speciation in soils and sediments. Talanta 2012;99:363-638.

353 [19] Reis AT, Coelho JP, Rucandio I, Davidson CM, Duarte AC, Pereira E. Thermo-
354 desorption: A valid tool for mercury speciation in soils and sediments?. Geoderma
355 2015;237-238:98-104.

356 [20] Rumayor M, Díaz-Somoano M, López-Antón MA, Ochoa-González R, Martínez-
357 Tarazona MR. Temperature programmed desorption as a tool for the identification of
358 mercury fate in WFGD systems.Fuel 2015;148:98-103.

359 [21] Rumayor M, Díaz-Somoano M, López-Antón MA, Martínez-Tarazona MR.
360 Mercury compounds characterization by thermal desorption. Talanta 2013;114:318-322.

361 [22] Coufalík P, Krásenský P, Dosbaba M, Komárek J. Sequential extraction and
362 thermal desorption of mercury from contaminated soil and tailings from Mongolia. Eur
363 J Chem 2012;10(5):1565-1573.

364 [23] López-Antón MA, Rumayor M, Díaz-Somoano M, Martínez-Tarazona MR.
365 Influence of a CO2-enriched flue gas on mercury capture by activated carbons. Chem
366 Eng J 2015;262:1237-1243.

367 [24] López-Antón MA, Tascón JMD, Martínez-Tarazona MR. Retention of mercury in
368 activated carbons in coal combustion and gasification flue gases. Fuel ProcessTechnol
369 2002;77-78:353-358.

370 [25] Rumayor M, López-Antón MA, Díaz-Somoano M, Martínez-Tarazona MR.
371 Device for identification of mercury species in solids. Consejo Superior de
372 Investigaciones Científicas (CSIC). 2015. Patent ES1641.1031. Application number:
373 P201530310

374 [26] Terzano R, Santoro A, Spagnuolo M, Vekemans B, Medici L, Janssens K,
375 Gottlicher J, Denecke MA, Mangold S, Ruggiero P. Solving mercury (Hg) speciation in
376 soil samples by synchrotron X-ray microspectroscopic techniques. Environ Pollut
377 2010;158:2702-2709.

378 [27] Kizil´shtein LY, Peretyat`ko AG, Gofen GI. Concentration of impurity elements in
379 coals from aspects of the concept of hard and soft acids and bases, Khim Tverd Topl .
380 Chem Solid Fuels 1989;23(2):132-138.

381 [28] Pavlish JH, Hamre LL, Zhuang Y. Mercury control technologies for coal
382 combustion and gasification systems. Fuel 2010;89:838-847.

383 [29] Reddy KSK, Shoaibi AA, Srinivasakannan C. Elemental mercury adsorption on
384 sulphur-impregnated porous carbon-A review. Environ Technol 2014;35:18-26.

385 [30] López-Antón MA, Abad-Valle P, Díaz-Somoano M, Martínez-Tarazona MR.
386 Evaluation of the variables that influence mercury capture in solid sorbents. CCGP
387 2009;1:32-37. (doi: 10.4177/CCGP-D-09-00007.1)

388

389 **Table 1.** Mercury, sulphur, chlorine and selenium contents of the coal samples

Sample name	Country	Coal	Hg $\mu g \cdot g^{-1}$	S %	Cl $\mu g \cdot g^{-1}$	Se $\mu g \cdot g^{-1}$
HL	Hungary	Lignite	0.21	2.3	34	0.3
CL-Sb	China	Lignite	0.11	0.5	34	2.6
SAL-SAB2	South Africa	Lignite	0.16	0.7	64	0.5
SL-Pe	Spain	Lignite	0.19	3.2	133	7.3
SB-Mo	Spain	Bituminous	0.29	0.9	950	1.4
SB-Mi	Spain	Bituminous	0.27	0.8	130	1.5
SB-Jo	Spain	Bituminous	1.52	2.2	60	2.0
SB-A	Spain	Bituminous	0.11	0.6	44	0.9
SB-C	Spain	Bituminous	0.12	1.7	52	2.2
SB-Ca	Spain	Bituminous	0.14	1.2	840	1.1
RB-Dia	Russia	Bituminous	0.17	0.4	50	0.2
RB-Si	Russia	Bituminous	0.08	0.3	10	0.1
COB-Be	Colombia	Bituminous	0.09	0.7	140	1.6
COB-Pa	Colombia	Bituminous	0.15	0.7	60	1.4
SAB-FB	South Africa	Bituminous	0.11	0.5	110	1.3
CSb-GZ	China	Sub-bituminous	0.28	5.3	ND	1.9
SA-T	Spain	Anthracite	0.21	1.1	703	0.6
SA-F	Spain	Anthracite	0.31	1.1	133	3.0

390 ND: not detected

Table 2. High peak temperatures of mercury compounds used as reference materials

	High peak Temperature (°C)
$HgCl_2$	135±5
Hg-FeS_2	169±5
Hg-OM	217±7
HgSe	260±6
HgS	303±13
HgO	(310±5);462±9
HgSO4	580±19

( ): minor peak

Table 3. Mercury species present in the coal samples

(%)	**$HgCl_2$**	**Hg-FeS_2**	**Hg-OM**	**HgS**	**HgSe**	**HgO**
HL	5.8	40.9	53.3	-	-	-
CL-Sb	5.2	26.0	36.6	16.1	16.1	-
SAL-SAB2	-	36.7	63.3	-	-	-
SL-Pe	1.1	19.9	45.5	22.1	-	11.4
SB-Mo	-	-	48.7	20.1	23.5	7.7
SB-Mi	-	-	53.9	13.1	30.8	2.2
SB-Jo	-	-	78.1	4.9	10.2	6.8
SB-A	-	-	38.7	26.3	28.2	6.8
SB-C	-	-	67.9	2.8	9.2	20.0
SB-Ca	-	-	54.3	16.2	21.6	7.9
RB-Dia	-	44.6	51.3	-	4.2	-
RB-Si	-	27.9	40.6	14.4	17.1	-
COB-Be	-	30.4	30.6	-	39.0	-
COB-Pa	-	-	100	-	-	-
SAB-FB	-	29.9	32.8	15.8	14.2	7.4
CSb-GZ	-	12.1	30.3	27.2	25.8	4.6
SA-T	-	-	1.8	69.6	-	28.5
SA-F	-	-	3.1	65.6	-	31.3

Figure captions

Figure 1. Configuration of the thermo-desorption device used for mercury speciation in coals.

Figure 2. Thermal profiles of lignites.

Figure 3. Thermal profiles of bituminous and sub-bituminous coals.

Figure 4. Thermal profiles of anthracites.

Figure 5. Thermal profiles of the RB3 activated carbon after it has been used as a mercury sorbent in N_2, oxy-combustion and air combustion atmospheres.

Figure 6. Thermal profiles of the RBHG3 activated carbon after it has been used as a mercury sorbent in N_2, oxy-combustion and air combustion atmospheres.

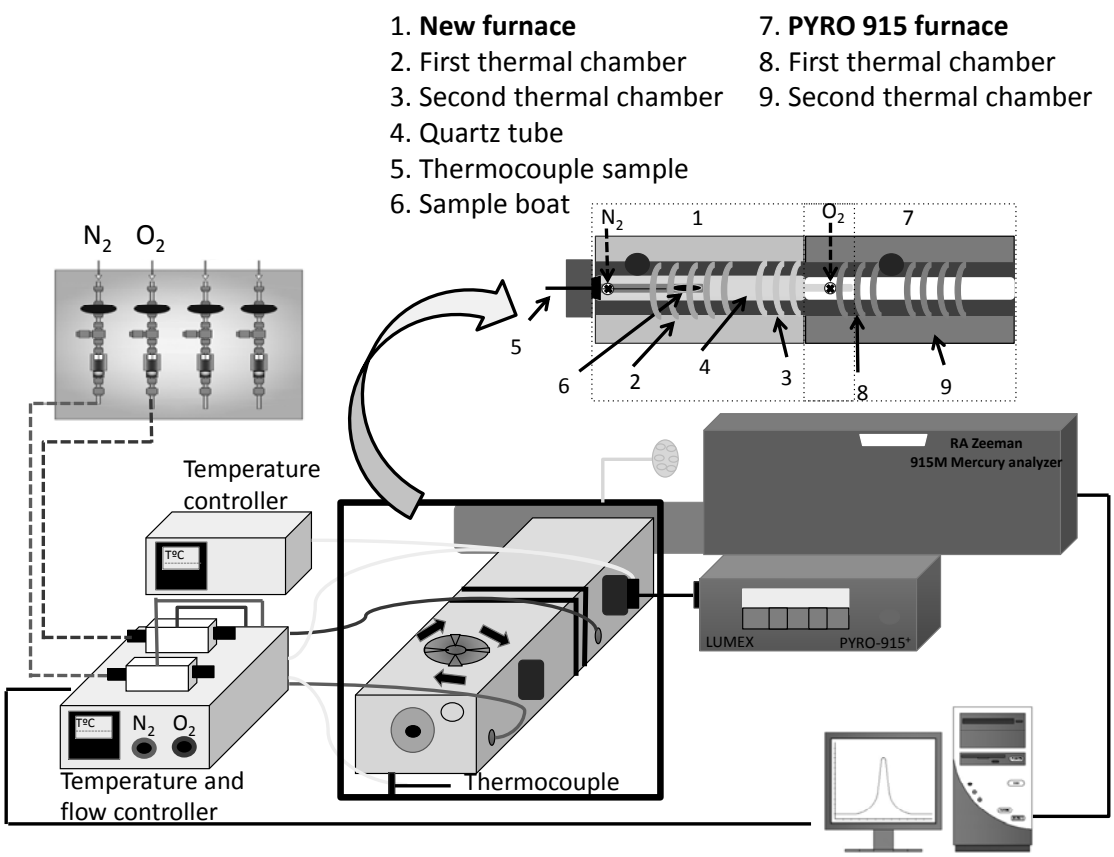
1. New furnace
2. First thermal chamber
3. Second thermal chamber
4. Quartz tube
5. Thermocouple sample
6. Sample boat
7. PYRO 915 furnace
8. First thermal chamber
9. Second thermal chamber
N2
O2
Temperature controller
Temperature and flow controller
Thermocouple
RA Zeeman 915M Mercury analyzer
LUMEX
PYRO-915+

Figure 1

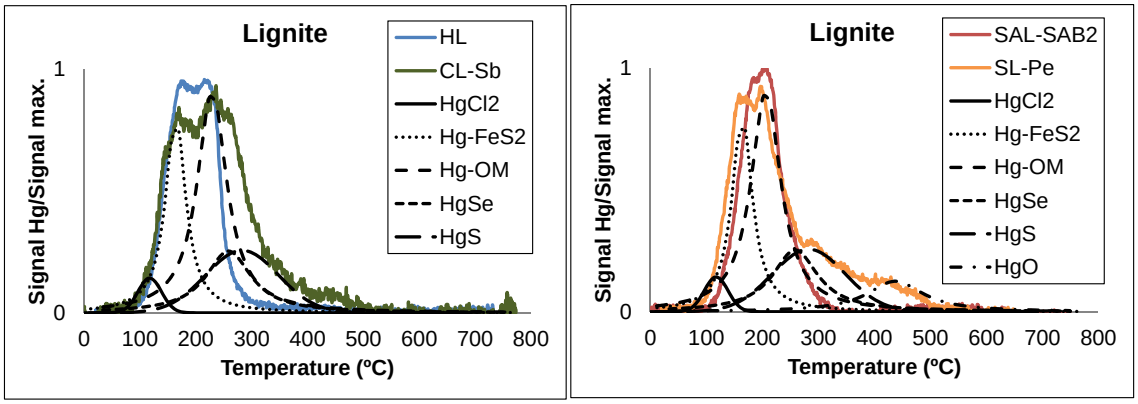
Lignite
HL
CL-Sb
HgCl2
Hg-FeS2
Hg-OM
HgSe
HgS
Signal Hg/Signal max.
1
0
0 100 200 300 400 500 600 700 800
Temperature (ºC)
Lignite
SAL-SAB2
SL-Pe
HgCl2
Hg-FeS2
Hg-OM
HgSe
HgS
HgO
Signal Hg/Signal max.
1
0
0 100 200 300 400 500 600 700 800
Temperature (ºC)

Figure 2

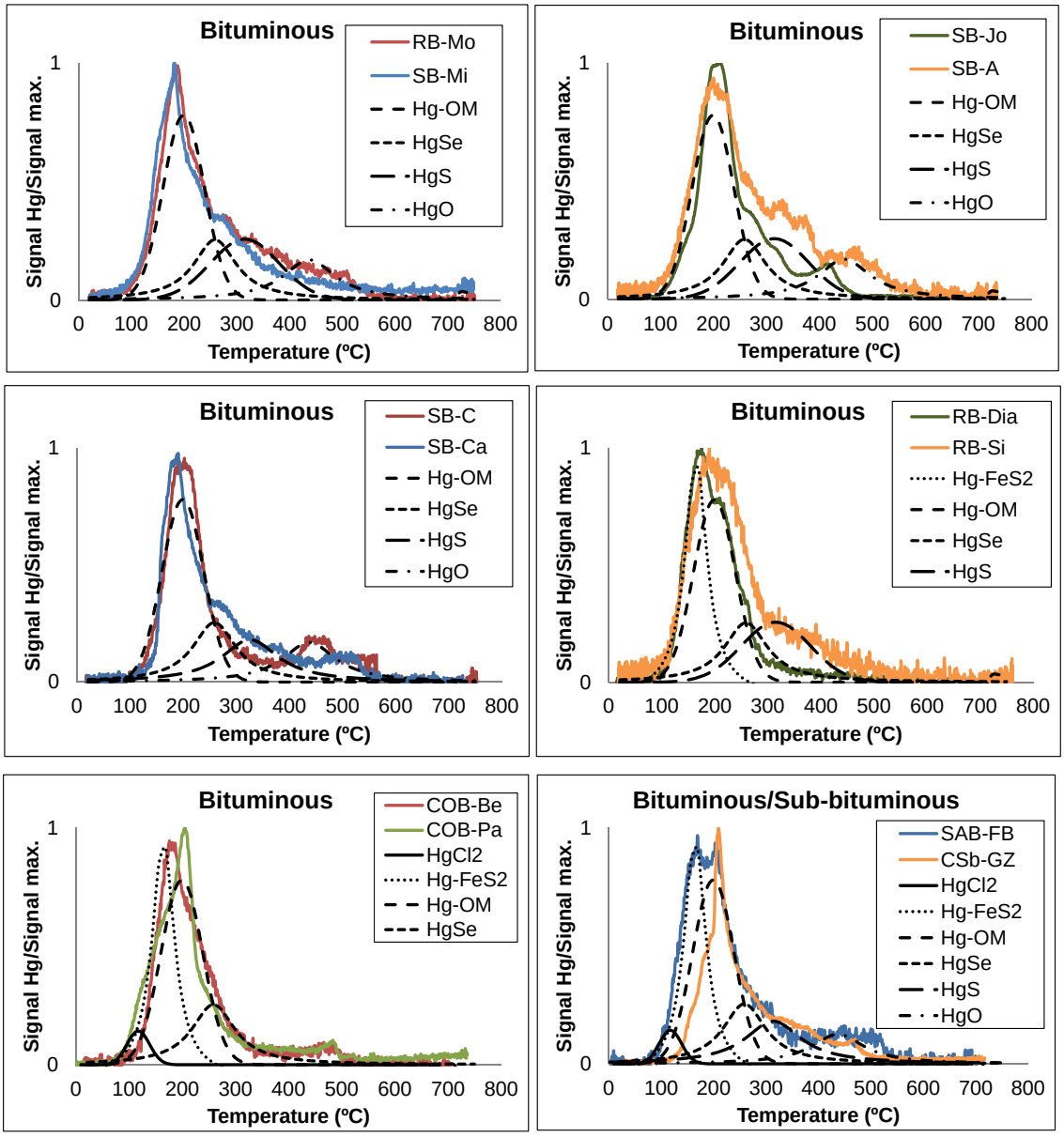
Bituminous
RB-Mo
SB-Mi
Hg-OM
HgSe
HgS
HgO
Signal Hg/Signal max.
Temperature (ºC)
Bituminous
SB-Jo
SB-A
Hg-OM
HgSe
HgS
HgO
Signal Hg/Signal max.
Temperature (ºC)
Bituminous
SB-C
SB-Ca
Hg-OM
HgSe
HgS
HgO
Signal Hg/Signal max.
Temperature (ºC)
Bituminous
RB-Dia
RB-Si
Hg-FeS2
Hg-OM
HgSe
HgS
Signal Hg/Signal max.
Temperature (ºC)
Bituminous
COB-Be
COB-Pa
HgCl2
Hg-FeS2
Hg-OM
HgSe
Signal Hg/Signal max.
Temperature (ºC)
Bituminous/Sub-bituminous
SAB-FB
CSb-GZ
HgCl2
Hg-FeS2
Hg-OM
HgSe
HgS
HgO
Signal Hg/Signal max.
Temperature (ºC)

Figure 3

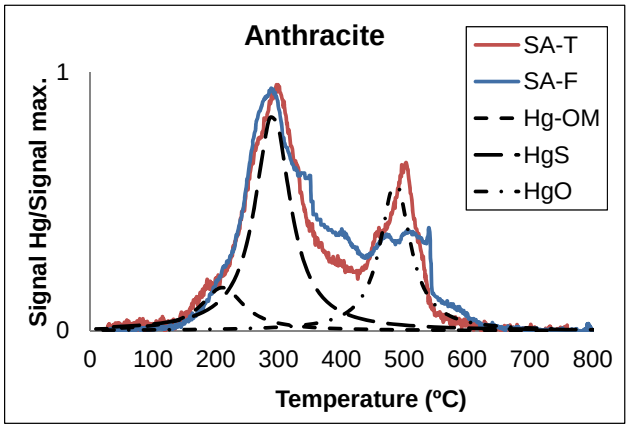
Anthracite
SA-T
SA-F
Hg-OM
HgS
HgO
Signal Hg/Signal max.
1
0
0
100
200
300
400
500
600
700
800
Temperature (ºC)

Figure 4

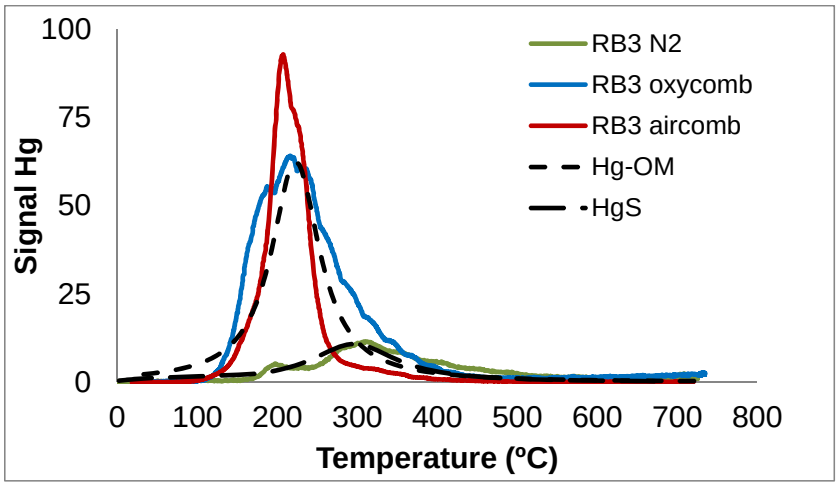

Figure 5

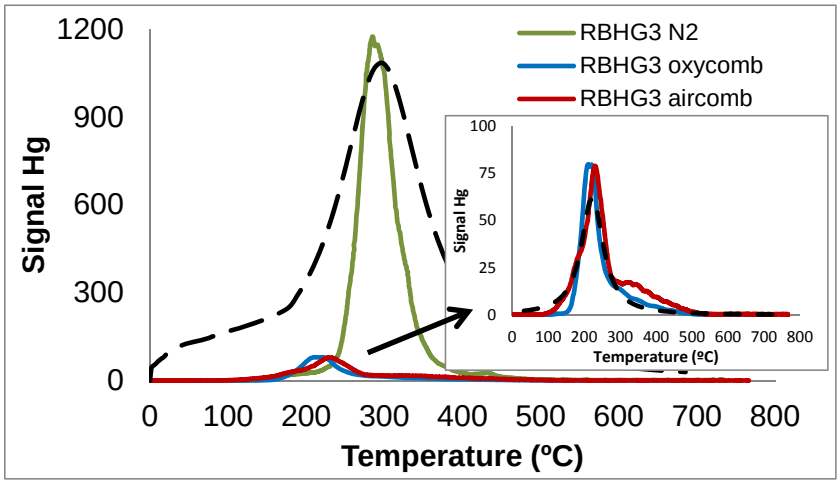

Figure 6